The Evaluation of Triphenyl Phosphate as a Flame Retardant Additive to Improve the Safety of Lithium-Ion Battery Electrolytes

M. C. Smart*, F. C. Krause †, C. Hwang*, W. C. West*, J. Soler*, G. K. S. Prakash †, and B. V. Ratnakumar*,

** Jet Propulsion Laboratory, California Institute of Technology*
4800 Oak Grove Drive, Pasadena, CA 91109-8099
† University of Southern California, Loker Hydrocarbon Research Institute
837 Bloom Walk, Los Angeles, CA 91003

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Outline

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- Experimental
- Approach and Methodology

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- Li metal-$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ Experimental Coin Cell Results
- Graphite-Toda $LiNiCoMnO_2$ Experimental Coin Cell Results
- Graphite-Toda $LiNiCoMnO_2$ Experimental 3-Electrode Cell Results
- Prototype Cell Results
  - MCMB-$LiNiCoO_2$ 7 Ah Cells Manufactured by Yardney Technical Products

- Conclusions

Introduction

- NASA is actively pursuing the development of advanced electrochemical energy storage and conversion devices for future lunar and Mars missions.

- The Exploration Technology Development Program, Energy Storage Project is sponsoring the development of ***advanced Li-ion batteries*** and PEM fuel cell and regenerative fuel cell systems for the Altair Lunar Lander, Extravehicular Activities (EVA), and rovers and as the primary energy storage system for Lunar Surface Systems.

- At JPL, in collaboration with NASA-GRC, NASA-JSC and industry, we are actively developing advanced Li-ion batteries with improved specific energy, energy density and safety. One effort is focused upon developing Li-ion battery electrolyte with enhanced safety characteristics (i.e., low flammability).

- A number of commercial applications also require Li-ion batteries with enhanced safety, especially for automotive applications.

Exploration Technology Development Program
Energy Storage Project

Exploration Technology Development Program

Multiple focused projects to develop enabling technologies addressing high priority needs for Lunar exploration. Matures technologies to the level of demonstration in a relevant environment – TRL 6

Energy Storage Project –

Developing electrochemical systems to address Constellation energy storage needs

Altair - Lunar Lander

- **Primary fuel cells – descent stage**
- **Secondary batteries – ascent stage**

EVA

- **Secondary batteries for the Portable Life Support System (PLSS)**

Lunar Surface Systems (LSS)

- **Regenerative fuel cell systems for surface systems**
- **Secondary batteries for mobility systems**

➢ These applications will require high energy density Li-ion batteries with improved safety characteristics.

Desired Properties of Lithium-Ion Electrolytes

- ***Electrolyte Selection Criteria***

➢ High conductivity over a wide range of temperatures
  - 1 mS cm-1 from –60 to 40^{o}C

➢ Wide liquid range (low melting point)
  - -60 to 75^{o}C

➢ Good electrochemical stability
  - Stability over wide voltage window (0 to 4.5V)
  - Minimal oxidative degradation of solvents/salts

➢ Good chemical stability

➢ Good compatibility with chosen electrode couple
  - Good SEI characteristics on electrode
  - Facile lithium intercalation/de-intercalation kinetics

➢ Good thermal stability

➢ Good low temperature performance throughout life of cell
  - Good resilience to high temperature exposure
  - Minimal impedance build-up with cycling and/or storage

➢ *In addition to meeting these criteria, the electrolyte solutions should be ideally have low flammability and be non-toxic !!*

Flame Retardant Additives in Li-ion Cells for Improved Safety Characteristics

- Modification of electrolyte is one of the least invasive and cost effective ways to improve the safety characteristics of Li-ion cells. Common approaches include:
  - Use of Redox shuttles (to improve safety on overcharge)
  - Ionic liquids (have inherently low flammability, due to low vapor pressure)
  - Lithium salt modification
  - Flame retardant additives
  - Use of non-flammable solvents (i.e., halogenated solvents)
- Of these approaches, the use of flame retardant additives has been observed to possess the least impact upon cell performance.

Previous Work on Flame Retardant Additives in Li-ion Batteries

- Most flame retardant additives utilized contain phosphorus
  - Aromatic and alkyl phosphates most common
    - Tradeoff exists between flame retarding capabilities and electrochemical stability
  - Halogenated phosphate compounds
    - Tris (2,2,2-trifluoroethyl) phosphate reported to be one of the most promising FRAs examined to date - excellent performance characteristics[1]
  - Other potential FRAs include:
    - Phosphites[1]- P(III) oxidation state may lead to improve stability and act as Lewis acid scavenger
    - Phosphonates[3]
    - Phosphoramides
    - Phosphazenes[4]

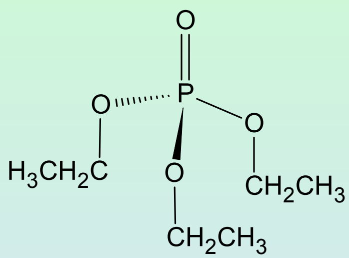
1) K. Xu, S. Zhang, J. L. Allen, T. R. Jow *J. Electrochem. Soc.*, **2002**, *149*, A1079

2) (a) S. S. Zhang, K. Xu, and T. R. Jow, *Journal of Power Sources* 113 (1), 166-172 (2003), (b) Nam, T.-H., Shim, E.-G., Kim, J.-G., Kim, H.-S., Moon, S.-I., *Journal of Power Sources* 180 (1), 561-567 (2008).

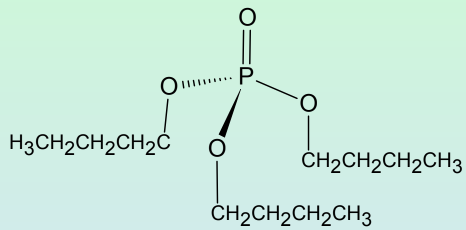
3) J. K. Feng, X. P. Ai, Y. L. Cao, and H. X. Yang, J. Power Sources, 177, 194-198 (2008).

4) T. Tsujikawa, K Yabuta, T. Matsushita, T. Matsushima, K. Hayashi, M. Arakawa, J. Power Sources, 189 (1) 429-434 (2009).

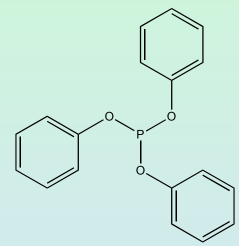
Development of Electrolytes Containing Flame Retardant Additives



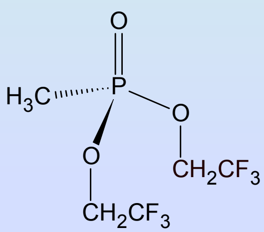
Triethyl phosphate (TEP)



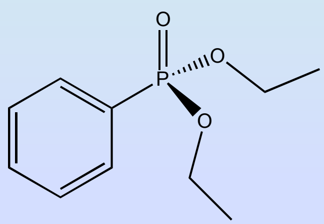
Tributyl phosphate (TBP)



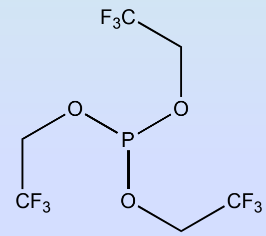
Triphenyl phosphite (TPPi)



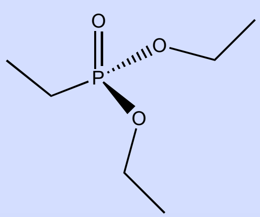
Bis-(2,2,2-trifluoroethyl)methyl phosphonate (BTFEMP)



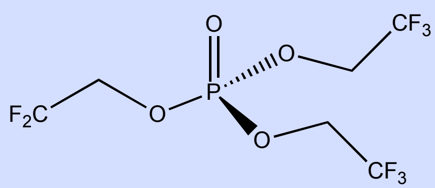
Diethyl phenylphosphonate (DPP)



Tris(2,2,2-trifluoroethyl) phosphite (TFPi)

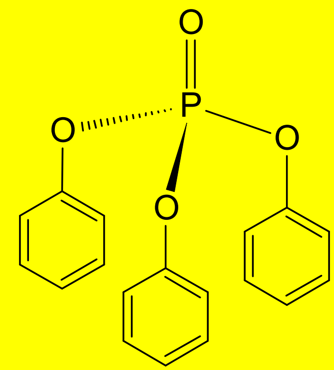


Diethyl ethylphosphonate (DEP)



Tris(2,2,2-trifluoroethyl) phosphate (TFPa)

TPP identified as being the most robust flame retardant additive



Triphenyl phosphate (TPP)

Electrolytes with the various additives were incorporated into three electrolyte cells with $LiNi_xCo_{1-x}O_2$ cathodes, MCMB anodes, and Li metal reference electrodes

1) Y. E. Hyung, D. R. Vissers, K. Amine
J. Power Sources, **2003**, *119-121*, 383

2) K. Xu, M. S. Ding, S. Zhang, J. L. Allen, T. R. Jow
J. Electrochem. Soc. **2002**, *149*, A622

Development of Electrolytes Containing Flame Retardant Additives

- Electrolytes and approaches investigated in NCA and NCO systems:

Varying Concentration of TPP

- 1.0M $LiPF_6$ EC+EMC+TPP (20:75:5 vol %)
- 1.0M $LiPF_6$ EC+EMC+TPP (20:70:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %)

Use of Fluorinated Linear Carbonates

- 1.0M $LiPF_6$ EC+EMC+DTFEC+TPP (20:50:20:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+DTFEC+TPP (20:30:40:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+TFEMC+TPP (20:50:20:10 vol %)

Use of Fluorinated Ethylene Carbonate

- 1.0M $LiPF_6$ FEC+EMC+TPP (20:70:10 vol %)
- 1.0M $LiPF_6$ FEC+EMC+TPP (20:65:15 vol %)
- 1.0M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 vol %)

Use of Additives (Vinylene Carbonate)

- 1.0M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 vol %) + 1.5% VC
- 1.0M $LiPF_6$ EC+EMC+TPP (20:75:5 vol %) + 1.5% VC
- 1.0M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %) + 1.5% VC
- 1.0M $LiPF_6$ FEC+EMC+TPP (20:65:15 vol %) + 1.5% VC

Where DTFEC = di-2,2,2-trifluoroethyl carbonate
TFEMC = 2,2,2-trifluoroethyl methyl carbonate
FEC = mono-fluoroethylene carbonate
TPP = triphenyl phosphate

Flammability tests have been performed on select samples by Prof. Lucht at Univ. Rhode Island

Electrolytes With Improved Safety and Good High Voltage Stability

Formation Characteristics of Three Electrode MCMB-$LiNi_xCo_{1-x}O_2$ Cells

Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreverisible Capacity (1st Cycle)	Couloumbic Efficiency (1st Cyle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreverisible Capacity (1st-5th Cycle)	Couloumbic Efficiency (5th Cycle)
1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %)	0.4980	0.4160	0.082	83.52	0.4119	0.4022	0.1264	97.64
1.0 M $LiPF_6$ EC+EMC (20:80 v/v %)	0.4504	0.3768	0.074	83.64	0.3799	0.3676	0.1356	96.75
1.0 M $LiPF_6$ EC+EMC+TPP (20:70:10 v/v %)	0.4705	0.3978	0.073	84.55	0.3969	0.3819	0.1449	96.20
1.0 M $LiPF_6$ EC+EMC+DTFEC+TPP (20:50:20:10 v/v %)	0.4929	0.4234	0.070	85.89	0.4248	0.4148	0.1157	97.64
1.0 M $LiPF_6$ EC+EMC+DTFEC+TPP (20:30:40:10 v/v %)	0.4904	0.4124	0.078	84.09	0.4272	0.4035	0.1958	94.45
1.0 M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 v/v %)	0.4391	0.3687	0.070	83.97	0.3698	0.3646	0.0967	98.60
1.0 M $LiPF_6$ FEC+EMC+TPP (20:70:10 v/v %)	0.4784	0.4095	0.069	85.59	0.4127	0.4063	0.1015	98.45
1.0 M $LiPF_6$ EC+EMC+TFEMC+TPP (20:50:20:10 v/v %)	0.4494	0.3753	0.074	83.51	0.3655	0.3596	0.1192	98.40
1.0 M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 v/v %) + 1.5% VC	0.4574	0.3868	0.071	84.55	0.3941	0.3867	0.1036	98.13

When the electrolytes were evaluated in MCMB-$LiNiCoO_2$ cells, generally good performance was observed with the electrolytes studied. However, some impact upon performance was observed with a high fluorinated carbonate content. This decrease in performance was not as dramatic as when the electrolytes were investigated in Li-$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ cells.

Advanced Low Temperature, Non-flammable Electrolytes

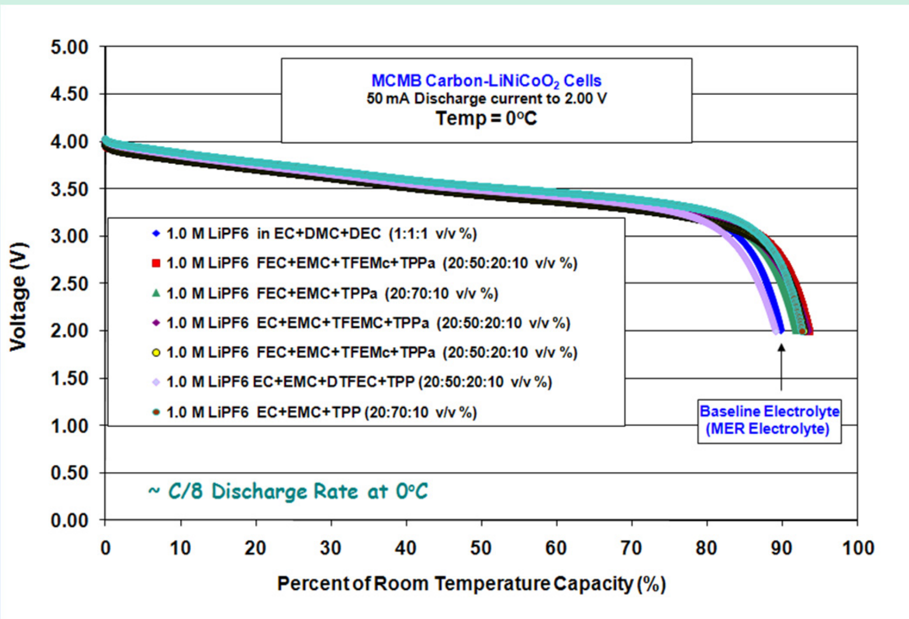
Summary Discharge Characteristics at Low Temperatures

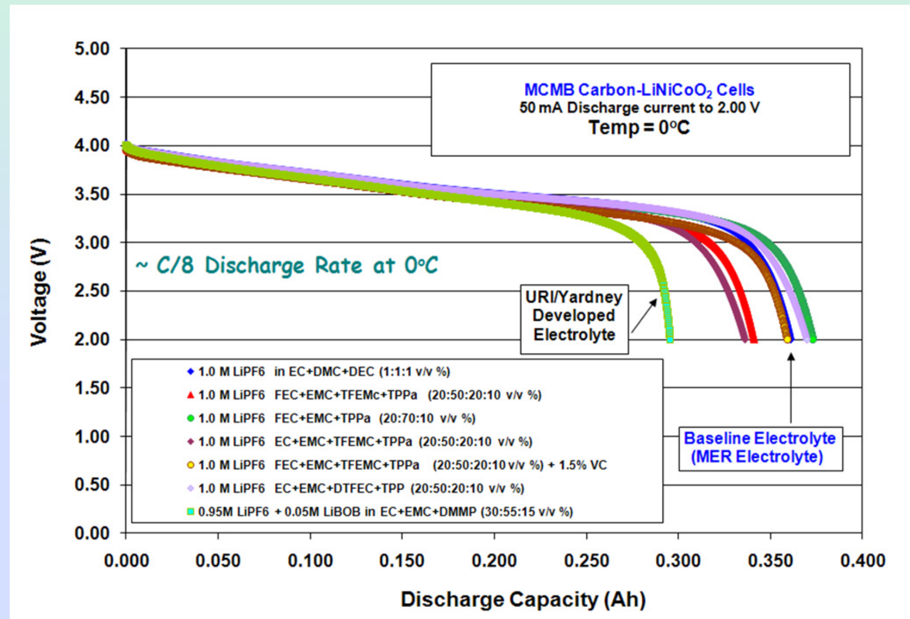
Electrolyte Type →		1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %)		1.0 M $LiPF_6$ FEC+EMC+TFEMC+TPPa (20:50:20:10 v/v %)		1.0 M $LiPF_6$ FEC+EMC+TPP (20:70:10 v/v %)		1.0 M $LiPF_6$ EC+EMC+TFEMC+TPP (20:30:40:10 v/v %)		1.0 M $LiPF_6$ FEC+EMC+TFEMC+TPPa (20:50:20:10 v/v %) + 1.5% VC	
Temp.	Current (mA)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)
23°C	25 mA	0.4022	100.00	0.3646	100.00	0.4063	100.00	0.3596	100.00	0.3867	100.00
0°C	25 mA	0.3633	90.31	0.3497	95.92	0.3805	93.63	0.3410	94.81	0.3621	93.64
	50 mA	0.3609	89.73	0.3409	93.48	0.3731	91.82	0.3362	93.47	0.3591	92.88
	100 mA	0.3199	79.55	0.3037	83.30	0.3374	83.04	0.2945	81.89	0.3207	82.93
	150 mA	0.2950	73.35	0.2539	69.62	0.3053	75.14	0.2298	63.89	0.2914	75.35
- 10°C	25 mA	0.3202	79.60	0.3148	86.33	0.3544	87.23	0.3158	87.82	0.3238	83.74
	50 mA	0.2974	73.95	0.2926	80.26	0.3216	79.15	0.3013	83.79	0.3071	79.41
	100 mA	0.2607	64.82	0.2026	55.57	0.2324	57.20	0.2144	59.60	0.2593	67.07
	150 mA	0.2182	54.25	0.0802	22.01	0.1793	44.14	0.1174	32.65	0.2219	57.38
- 20°C	25 mA	0.2723	67.70	0.2982	81.79	0.3388	83.39	0.3010	83.68	0.3127	80.88
	50 mA	0.2313	57.51	0.2458	67.40	0.2876	70.79	0.2544	70.73	0.2728	70.54
	100 mA	0.0661	16.43	0.0772	21.18	0.1670	41.10	0.0778	21.62	0.1694	43.81
	150 mA	0.0312	7.77	0.0287	7.88	0.0411	10.12	0.0272	7.57	0.0493	12.76
- 30°C	25 mA	0.0288	7.16	0.2467	67.67	0.2844	69.99	0.2654	73.79	0.2664	68.90
	50 mA	0.0198	4.93	0.1069	29.31	0.1979	48.71	0.1178	32.74	0.2050	53.03
- 40°C	25 mA	0.0203	5.06	0.0759	20.82	0.1611	39.64	0.0511	14.21	0.1673	43.27
- 50°C	25 mA	0.0059	1.46	0.0000	0.01	0.0377	9.27	0.0135	3.75	0.0234	6.04

Some formulations investigated have up to 40% of a partially fluorinated solvent and 10% flame retardant additive

Electrolytes With Improved Safety and Good High Voltage Stability

Discharge Characteristics of Three Electrode MCMB-$LiNi_xCo_{1-x}O_2$ Cells



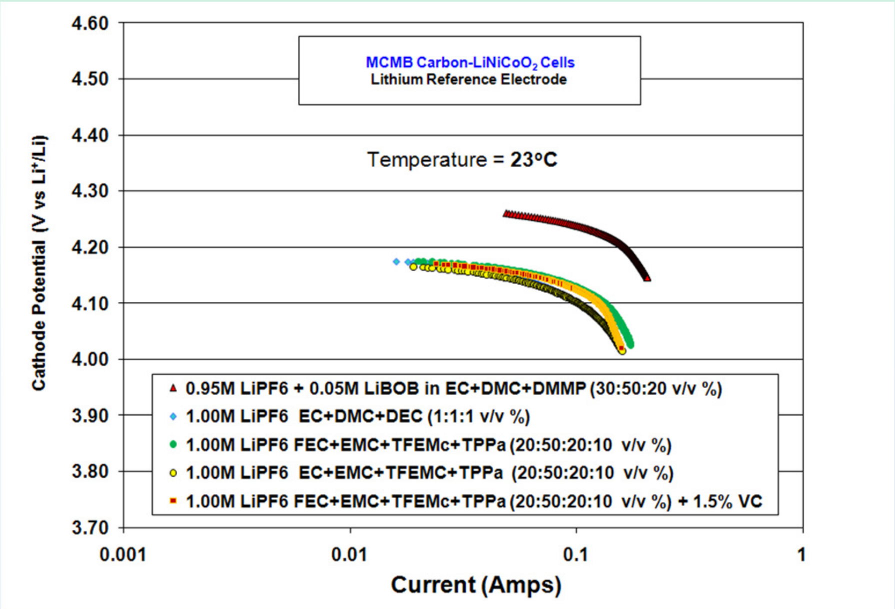


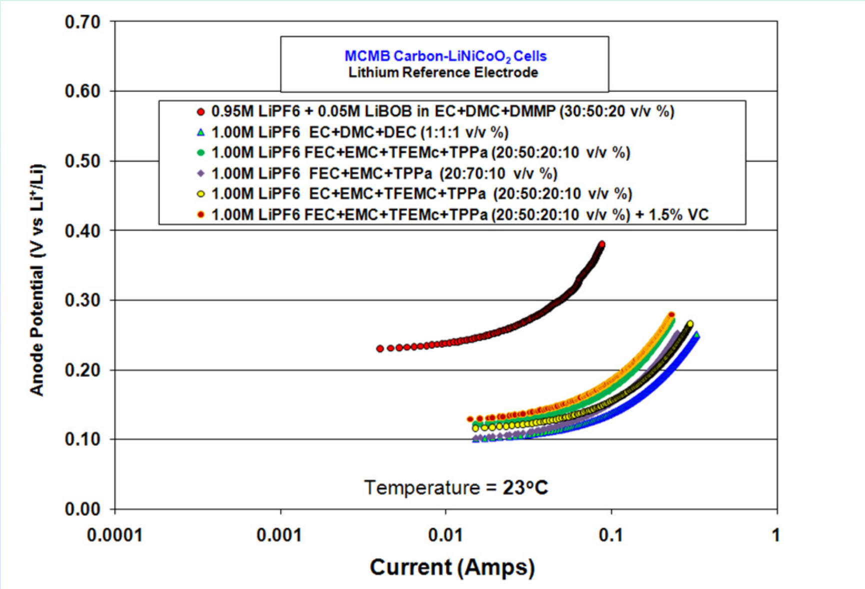
When the electrolytes were evaluated in MCMB-$LiNiCoO_2$ cells, generally good performance was observed with the electrolytes studied. Good performance was even observed when the EC was replaced completely with FEC and TFEMC was added as well at a ~ **C/4 rate at 0°C.**

For details regarding the URI/Yardney electrolyte see:
S. Dalavi, M. Xu, B. Ravdel, L. Zhou, and B. L. Lucht, *J. Electrochem. Soc.*, **157**, A1113 (2010).

Electrolytes With Improved Safety and Good High Voltage Stability

Tafel Characteristics of Three Electrode MCMB-$LiNi_xCo_{1-x}O_2$ Cells





- Performance of Yardney/URI electrolyte compared with baseline solution.
- Although lithium kinetics are observed to be facile at the cathode with the cell containing the Yardney/URI electrolyte, the lithium kinetics at the anode are dramatically lower compared with the baseline system.

Electrolytes With Improved Safety and Good High Voltage Stability

Formation Characteristics of Three Electrode Graphite-$LiNi_xCo_{1-x}AlO_2$ Cells

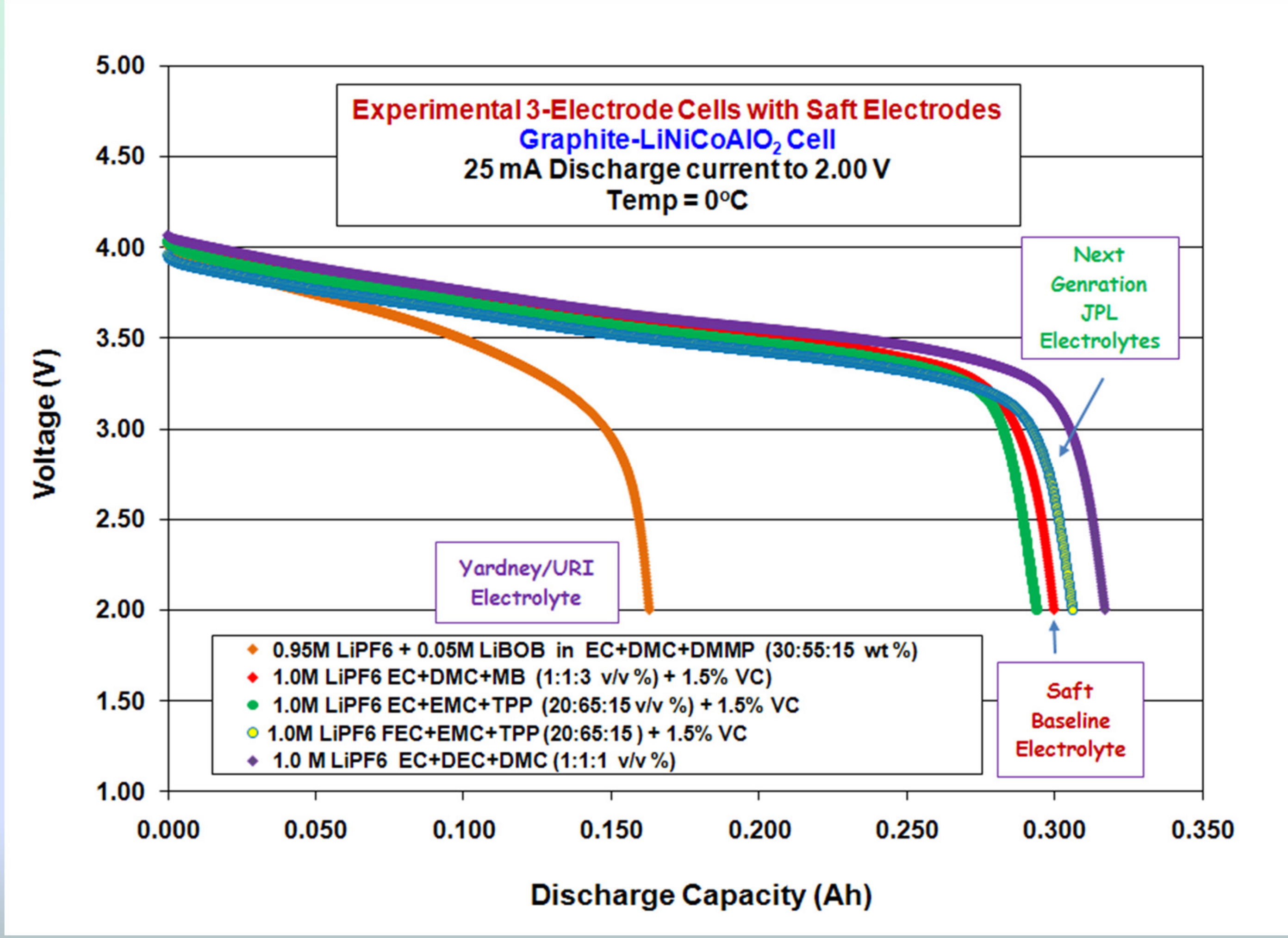
Saft Baseline Electrodes

Cell Number	Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreverisible Capacity (1st Cycle)	Couloumbic Efficiency (1st Cyle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreverisible Capacity (1st-5th Cycle)	Couloumbic Efficiency (5th Cycle)	Cathode Weight (g) (Including Substrate and Inactive Material)	Anode Weight (g) (Including Substrate and Inactive Material)
Cell ST07	0.95 M $LiPF_6$ + 0.05M LiBOB in EC+DMC+DMMP (30:55:15 v/v %)	0.4608	0.3084	0.152	66.92	0.2842	0.2036	0.4300	71.62	3.068	2.454
Cell ST08	1.0 M $LiPF_6$ EC+DMC+MB (1:1:3 v/v %) + 1.5% VC	0.4737	0.4124	0.061	87.06	0.3713	0.3620	0.0986	97.49	3.066	2.453
Cell ST09	1.0 M $LiPF_6$ EC+EMC+TPP (20:65:15 v/v %) + 1.5% VC	0.4409	0.3715	0.069	84.26	0.3779	0.3673	0.1191	97.20	3.055	2.451
Cell ST10	1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %)	0.4306	0.3600	0.071	83.59	0.3609	0.3526	0.1048	97.71	2.944	2.445
Cell ST11	0.95 M $LiPF_6$ + 0.05M LiBOB in EC+DMC+DMMP (30:55:15 v/v %) [Final Delivery 12-2009]	0.4336	0.2684	0.165	61.91	0.2193	0.2025	0.2665	92.34	3.000	2.448
Cell ST12	1.0 M $LiPF_6$ FEC+EMC+TPP (20:65:15 v/v %) + 1.5% VC	0.4376	0.3689	0.069	84.31	0.3675	0.3688	0.0689	100.34	2.934	2.434

Electrolytes With Improved Safety and Good High Voltage Stability

Formation Characteristics of Three Electrode Graphite-$LiNi_xCo_{1-x}AlO_2$ Cells

Saft Baseline Electrodes



Electrolytes With Improved Safety and Good High Voltage Stability

Formation Characteristics of Three Electrode Graphite-$LiNi_xCo_{1-x}AlO_2$ Cells

Saft Baseline Electrodes

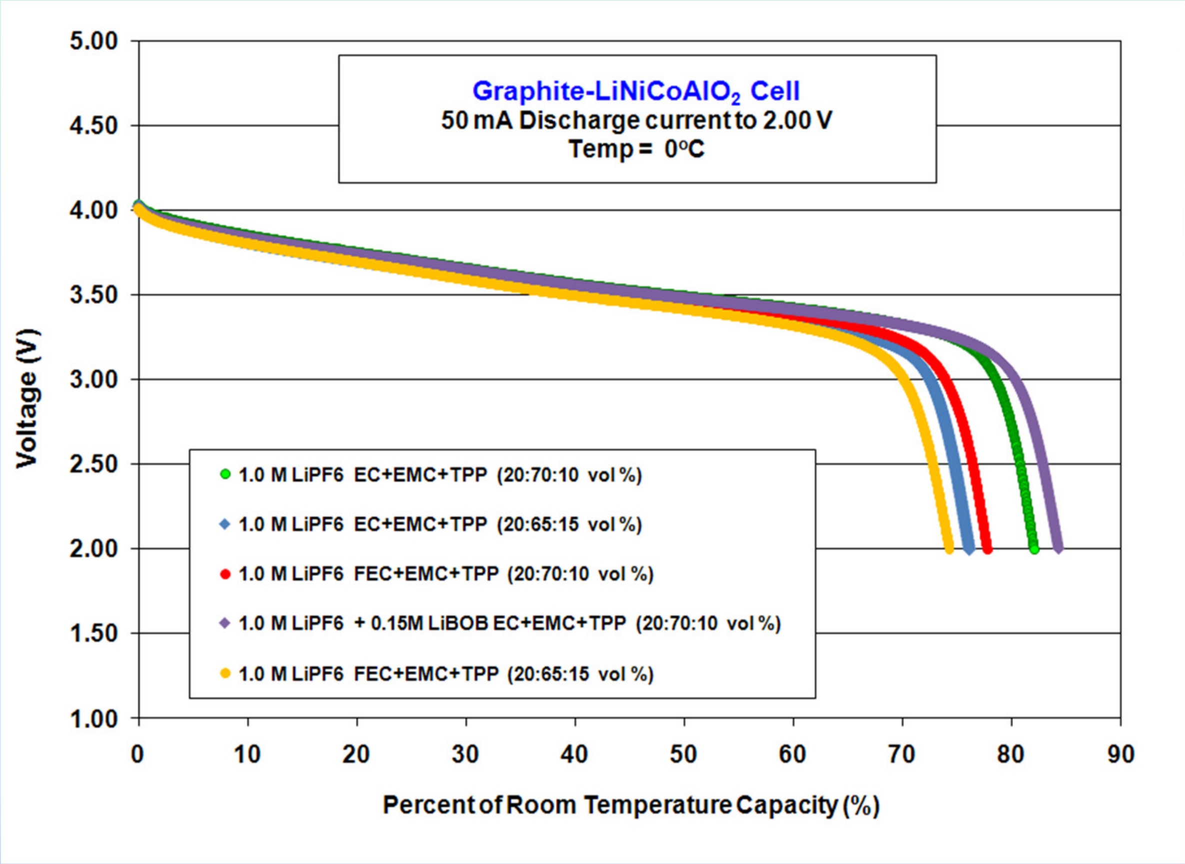
			ST13		ST14		ST15		ST16		ST17	
Electrolyte Type			1.00M $LiPF_6$ EC+EMC+TPP (20:70:10 vol %)		1.00M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %)		1.00M $LiPF_6$ FEC+EMC+TPP (20:70:10 vol %)		1.0M $LiPF_6$ + 0.15M LiBOB EC+EMC+TPP (20:70:10 vol %)		1.0 M LiPF6 FEC+EMC+TPP (20:65:15 vol %)	
Temp.	Current (mA)	Rate	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)
23°C	7.50 mA	C/65	0.5134	100.00	0.4991	100.00	0.5302	100.00	0.5253	100.00	0.5415	100.00
	25 mA	C/20	0.4888	95.19	0.4783	95.83	0.4922	92.83	0.5104	97.18	0.5203	96.08
	50 mA	C/10	0.4589	89.37	0.4440	88.95	0.4537	85.57	0.4881	92.93	0.4498	83.07
	100 mA	C/5	0.4046	78.81	0.3722	74.58	0.3881	73.20	0.4300	81.86	0.2867	52.95
	150 mA	C/3.3	0.3805	74.12	0.3203	64.18	0.3643	68.70	0.4015	76.44	0.2273	41.98
0°C	25 mA	C/20	0.4060	79.08	0.3877	77.68	0.3944	74.37	0.4308	82.02	0.3512	64.85
	50 mA	C/10	0.4213	82.06	0.3800	76.14	0.4123	77.76	0.4430	84.34	0.4024	74.31
	100 mA	C/5	0.3647	71.04	0.2428	48.65	0.3563	67.20	0.3926	74.74	0.2101	38.79
	150 mA	C/3.3	0.2897	56.41	0.1132	22.69	0.3201	60.38	0.3414	65.00	0.0823	15.20
- 20°C	25 mA	C/20	0.3499	68.15	0.2838	56.87	0.3294	62.13	0.3362	64.01	0.2291	42.31
	50 mA	C/10	0.2750	53.57	0.0975	2.00	0.2844	53.64	0.2631	50.10	0.0752	13.88
	100 mA	C/5	0.1027	19.99	0.0338	6.76	0.1365	25.74	0.1233	23.48	0.0207	3.83
	150 mA	C/3.3	0.0551	10.73	0.0217	4.34	0.0474	8.94	0.0687	13.08	0.0133	2.46

Electrolytes With Improved Safety and Good High Voltage Stability

Formation Characteristics of Three Electrode Graphite-$LiNi_xCo_{1-x}AlO_2$ Cells

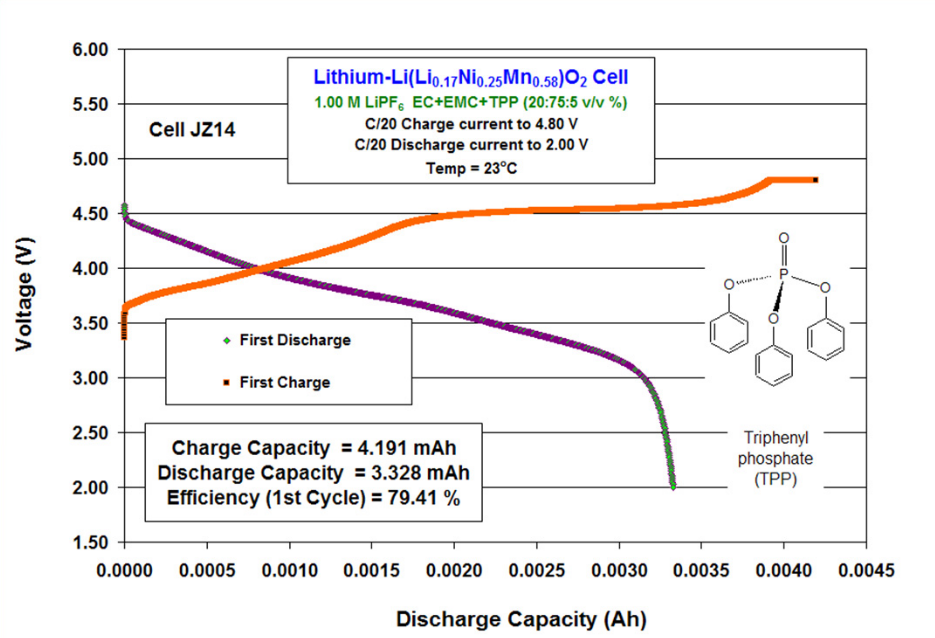
Saft Baseline Electrodes

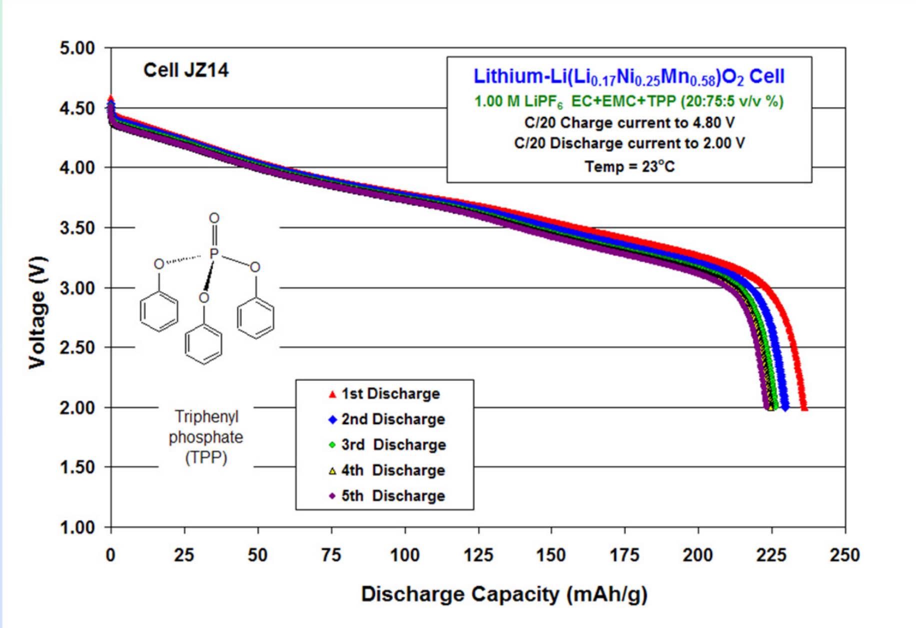
Comparison of Electrolyte Types = 50mA at 0°C



Electrolytes With Improved Safety and High Voltage Stability

Electrolyte = 1.0M $LiPF_6$ EC+EMC+TPP (20:75:5 v/v %)





Good performance is observed with the electrolyte containing the triphenyl phosphate FRA. Five formation cycles were performed on the cell, which displayed good reversibility.

Electrolytes With Improved Safety and High Voltage Stability

Li-Li($Li_{0.17}Ni_{0.25}Mn_{0.58}$)$O_2$ cells = Rate Capability at Low Temperature

		0.95 M $LiPF_6$ + 0.05M LiBOB EC+EMC+DMMP (30:55:15 v/v %)						1.0 M $LiPF_6$ EC+DEC+ DMC (1:1:1 v/v %)					
		Cell JZ41			JZ42			Cell JZ35			JZ36		
Temp (°C)	Discharge Rate	Ah	mAh/g	% of C/20 Capacity (mAh/g)	Ah	mAh/g	% of C/20 Capacity (mAh/g)	Ah	mAh/g	% of C/20 Capacity (mAh/g)	Ah	mAh/g	% of C/20 Capacity (mAh/g)
23°C	C/20	0.003109	233.76	100	0.003011	231.62	100	0.002721	226.77	100	0.002709	227.28	100
	C/10	0.002999	225.47	96.46	0.002942	226.32	97.71	0.002636	219.64	96.86	0.002626	220.34	96.94
	C/5	0.002816	211.71	90.57	0.002813	216.36	93.41	0.00251	209.18	92.25	0.0025	209.72	92.27
	C/2	0.002468	185.57	79.39	0.002496	192.02	82.91	0.002283	190.28	83.91	0.002122	178.00	78.32
0°C	C/20	0.002484	186.75	79.89	0.002425	186.57	80.55	0.002147	178.92	78.90	0.002102	176.34	77.59
	C/10	0.002278	171.31	73.28	0.002258	173.68	74.99	0.002051	170.94	75.38	0.001993	167.17	73.55
	C/5	0.001957	147.17	62.96	0.001981	152.36	65.78	0.001881	156.73	69.11	0.001678	140.80	61.95
	C/2	0.001558	117.14	50.11	0.001587	122.04	52.69	0.001416	118.04	52.05	0.000877	73.55	32.36
-10°C	C/20	0.002077	156.17	66.81	0.002034	156.48	67.56	0.001947	162.25	71.55	0.001876	157.41	69.26
	C/10	0.001925	144.74	61.92	0.001919	147.59	63.72	0.001744	145.30	64.08	0.001651	138.51	60.94
	C/5	0.001526	114.70	49.07	0.001538	118.27	51.06	0.00141	117.47	51.80	0.001065	89.31	39.29
	C/2	0.001052	79.12	33.85	0.001059	81.46	35.17	0.000658	54.84	24.18	0.000651	54.59	24.02

When the electrolytes were investigated in Li-Li($Li_{0.17}Ni_{0.25}Mn_{0.58}$)$O_2$ cells, comparable performance was observed with Yardney formulation compared with the baseline electrolyte (in terms of mAh/g). However, different trends may be observed when coupled with carbon anodes, rather than with lithium metal (i.e., due to the reactivity of LiBOB and/or DMMP).

Electrolytes With Improved Safety and High Voltage Stability

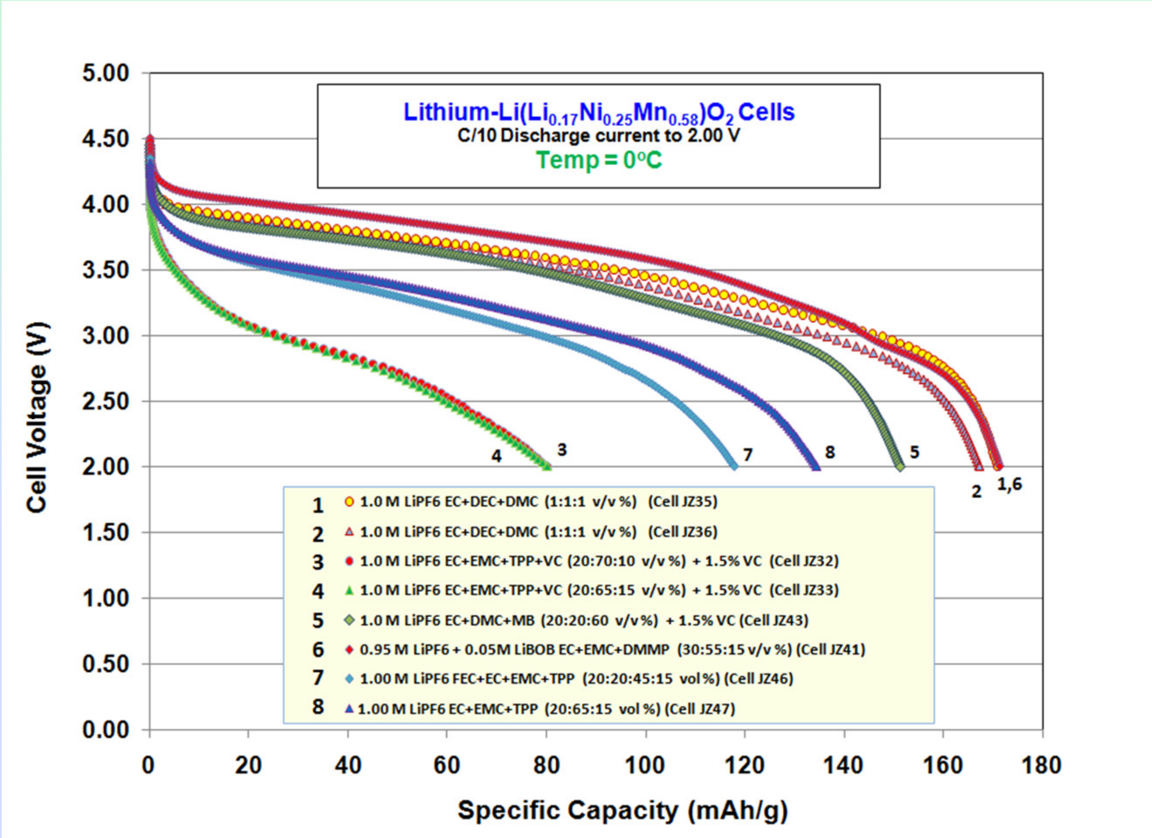
$Li\text{-}Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ cells = Rate Capability at Low Temperature

		1.0 M $LiPF_6$ FEC+EC+EMC+TPP (20:20:45:15 v/v %)						1.0 M $LiPF_6$ EC+EMC+TPP (20:65:15 v/v %)					
		Cell JZ45			JZ46			Cell JZ47			JZ48		
Temp (°C)	Discharge Rate	Ah	mAh/g	% of C/20 Capacity (mAh/g)	Ah	mAh/g	% of C/20 Capacity (mAh/g)	Ah	mAh/g	% of C/20 Capacity (mAh/g)	Ah	mAh/g	% of C/20 Capacity (mAh/g)
23°C	C/20	0.002549	205.56	100	0.002533	205.96	100	0.002528	210.65	100	0.002869	227.71	100
	C/10	0.002432	196.15	95.42	0.002437	198.14	96.20	0.002449	204.08	96.88	0.00252	199.98	87.82
	C/5	0.002228	179.65	87.39	0.002226	180.97	87.87	0.002328	194.01	92.10	0.002384	189.21	83.09
	C/2	0.001307	105.38	51.26	0.001463	118.98	57.77	0.001996	166.33	78.96	0.002064	163.79	71.93
0°C	C/20	0.001774	143.05	69.59	0.001771	143.97	69.90	0.001833	152.75	72.51	0.001827	144.96	63.66
	C/10	0.001459	117.63	57.22	0.00145	117.89	57.24	0.001614	134.50	63.85	0.001565	124.21	54.55
	C/5	0.000815	65.74	31.98	0.000812	66.00	32.05	0.001042	86.82	41.21	0.000952	75.59	33.20
	C/2	0.000287	23.13	11.25	0.000304	24.75	12.02	0.000395	32.88	15.61	0.000352	27.96	12.28
-10°C	C/20	0.000991	79.90	38.87	0.000954	77.60	37.68	0.001214	101.20	48.04	0.001108	87.90	38.60
	C/10	0.000727	58.59	28.50	0.000739	60.09	29.17	0.000942	78.46	37.25	0.000373	29.57	12.98
	C/5	0.000302	24.36	11.85	0.00031	25.18	12.23	0.00039	32.49	15.42	0.000329	26.11	11.47
	C/2	0.000134	10.82	5.27	0.000137	11.13	5.40	0.000158	13.17	6.25	0.000156	12.35	5.43
-20°C	C/20	0.000356	28.73	13.98	0.001138	92.55	44.94	0.000467	38.94	18.48	0.000425	33.74	14.82

When the electrolytes were investigated in $Li\text{-}Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ cells, reduced rate capability was observed with 20% EC+20% FEC+15%TPP.

Electrolytes With Improved Safety and High Voltage Stability

Li-Li($Li_{0.17}Ni_{0.25}Mn_{0.58}$)$O_2$ cells = Rate Capability at Low Temperature



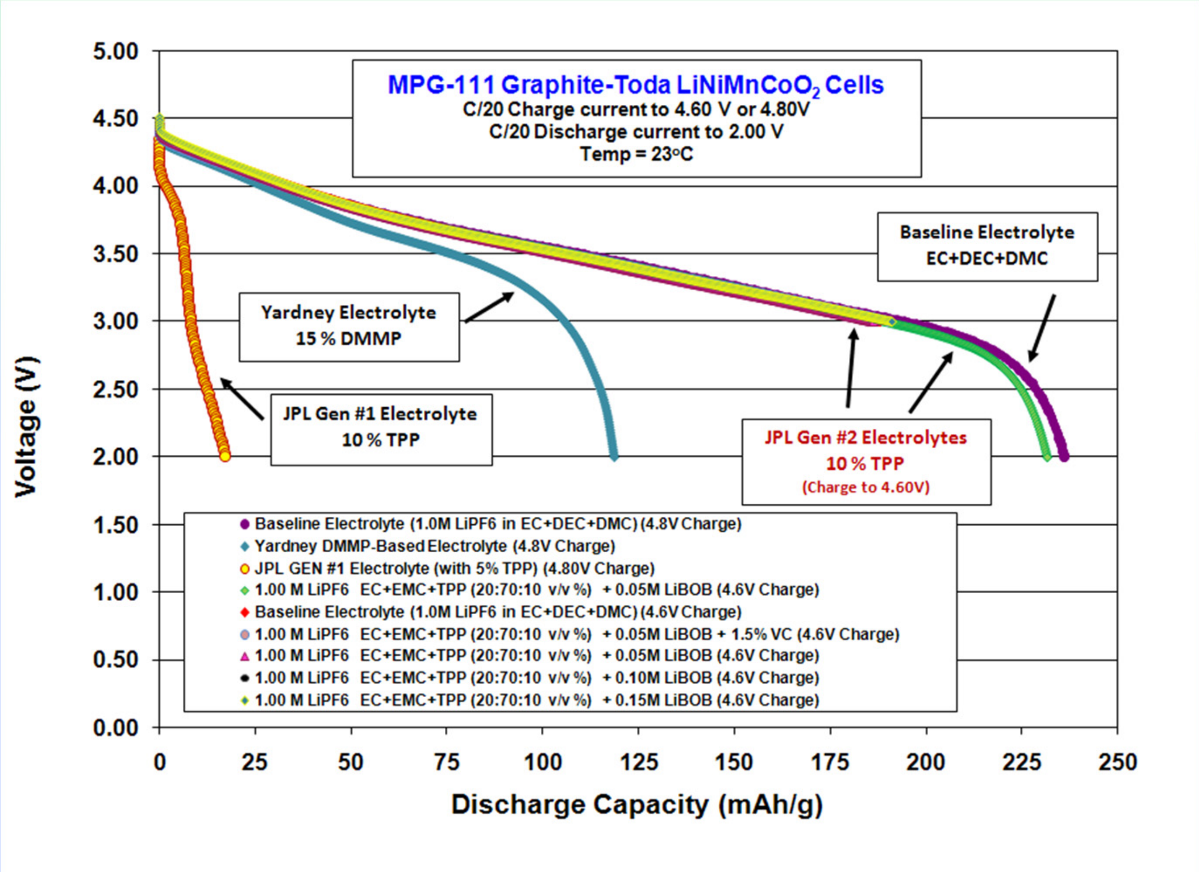
➢The URI/Yardney electrolyte performs very well with the NEI-D cathode, but much poorer when evaluated with carbon electrodes.

➢ High TPP content (with and without FEC and/or VC) appears to perform well in cells with carbonaceous anodes, but some performance decline observed when coupled with high voltage cathode (i.e., in Li/NEI-D cells).

➢*However, when these electrolytes were evaluated in the MPG-111/Toda cathode system, the performance was very poor necessitating further development. This lead to further modifications to the electrolytes !!*

Results from Second Batch of Electrolytes Evaluated in the MPG-111-Toda System

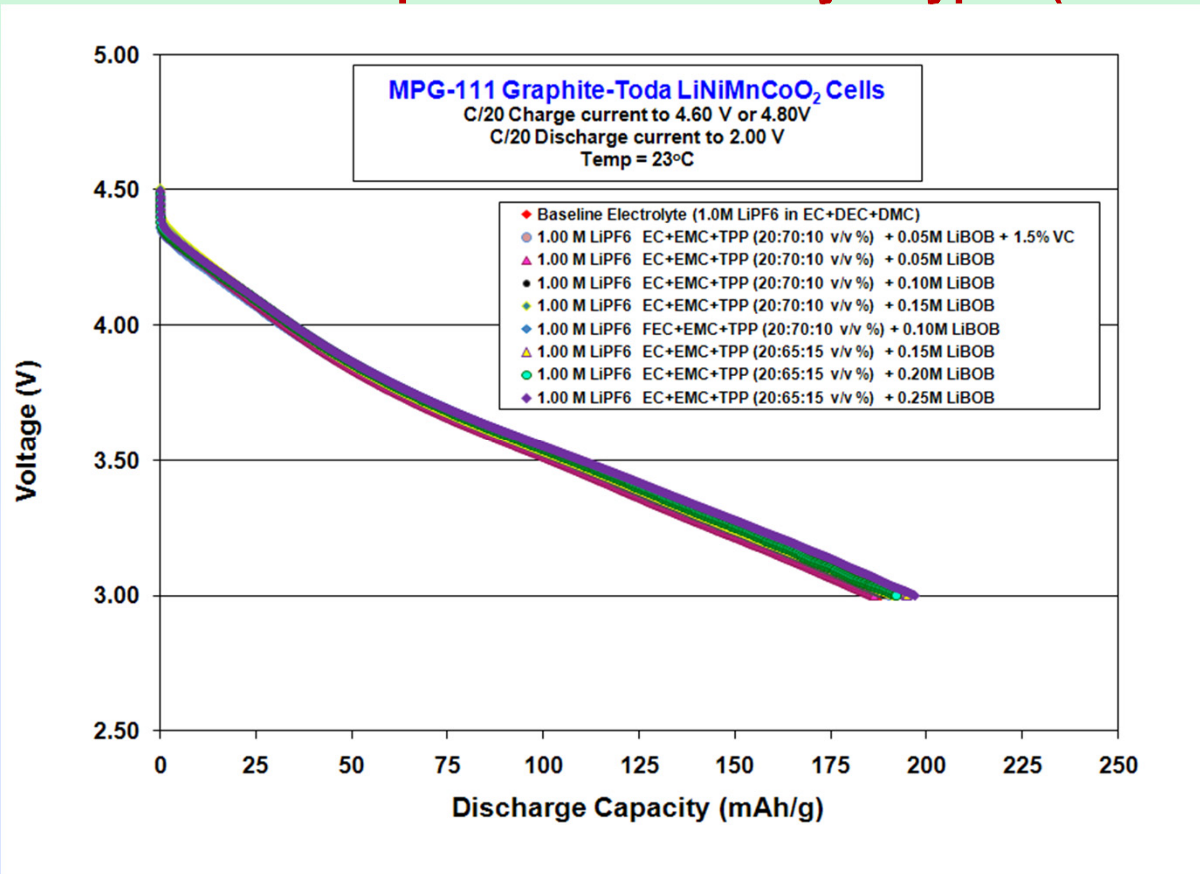
Comparison of Electrolyte Types (After Formation)



- *Comparable performance was obtained with the JPL Gen #2 electrolytes (containing LiBOB) compared with the baseline solution.*
- *There is no observed capacity (or voltage) benefit observed with charging to 4.80V*

Results of Electrolytes Evaluated in the MPG-111-Toda System

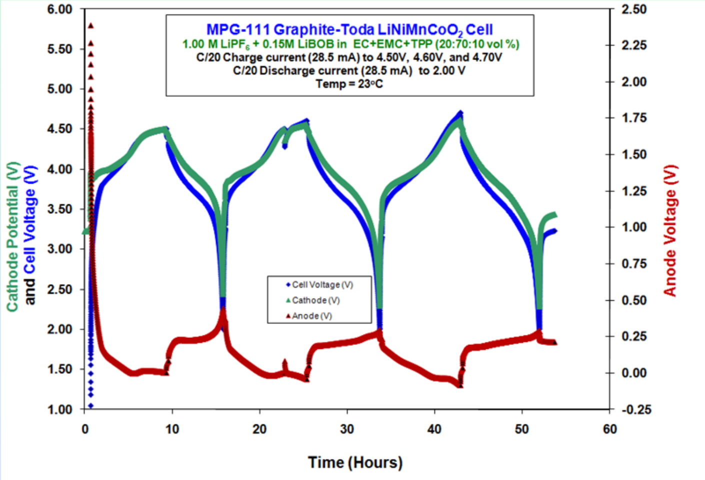
Comparison of Electrolyte Types (After Formation)

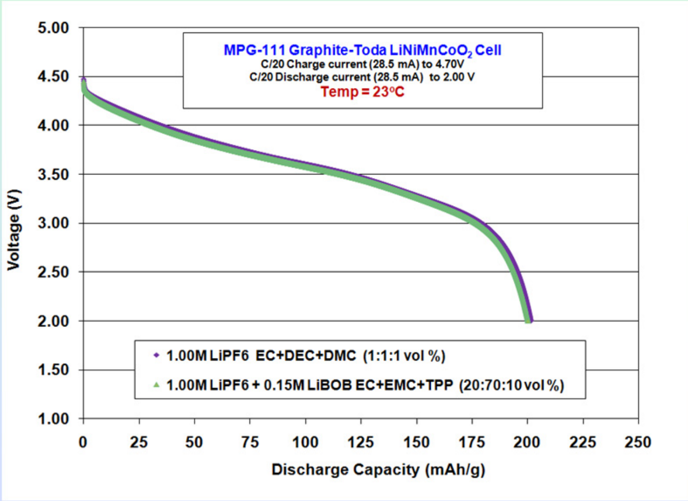


On-going work to identify further improvements (i.e., increasing TPP content and varying LiBOB concentrations)

- *A number of electrolytes displayed comparable performance with the the baseline solution, including the JPL Gen #2 electrolyte as well as newer iterations with increased TPP content (15%) and an FEC-containing blend.*
- *Cell cycled over the voltage range of 3.00 to 4.60V.*

Formation Characteristics of MPG-111-Toda Experimental Cells
Discharge Capacity





- Nearly identical reversible capacity was obtained with both electrolytes types.
- The discharge voltage profiles are very similar also.

Cell TM01
Baseline Electrolyte

Cycle #	Charge (Ah)	Discharge Capacity (Ah)	Irreversible Capacity (Ah)	Efficiency (%)	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)
1	0.28674	0.20135	0.085	70.22	162.38	68.86
2	0.25745	0.23368	0.024	90.77	188.45	19.17
3	0.25257	0.24971	0.003	98.86	201.38	2.31

Cumulative Irreversible Capcity Loss = 0.1120 Ah
Cumulative Irreversible Capcity Loss = 90.34 mAh/g

Cell TM02
JPL Generation II Electrolyte

Cycle #	Charge (Ah)	Discharge Capacity (Ah)	Irreversible Capacity (Ah)	Efficiency (%)	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)
1	0.24729	0.17637	0.071	71.32	142.35	57.19
2	0.26617	0.22849	0.038	85.84	184.41	30.39
3	0.25655	0.24780	0.009	96.59	200.00	7.06

Cumulative Irreversible Capcity Loss = 0.11735 Ah
Cumulative Irreversible Capcity Loss = 94.64 mAh/g

Performance Testing of Aerospace Quality Prototype Li-Ion Cells

Performance of Advanced Electrolytes in 7Ah Cells

- **Obtained a 7 Ah cells (NCP 7) fabricated by Yardney Technical Products containing JPL developed electrolytes:**

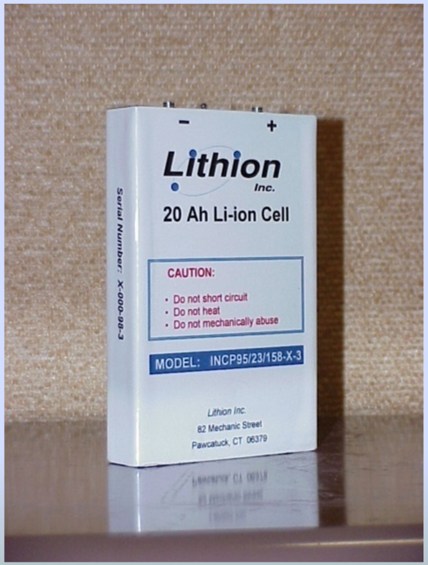
1.0 M $LiPF_6$ EC+EMC+TPP+VC (20:74:5:1.5 v/v %) (TPP = triphenyl phosphate)

1.0 M $LiPF_6$ EC+EMC+TFEB (20:60:20 v/v %) (TFEB=2,2,2-trifluoroethyl butyrate)

1.0 M $LiPF_6$ EC+EMC (20:80 v/v %)
1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %)
1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/ %) (Baseline – 2003 MER Rover Electrolyte)

Test Plan

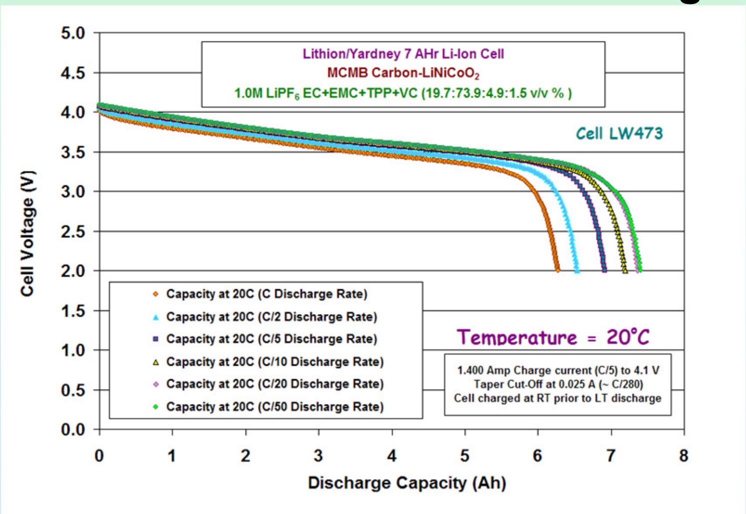
- Performed a number of performance evaluation tests
  - *Conditioning cycling performed at 20°, 0°, and -20°C (with impedance)*
  - *Discharge Rate Characterization at Various Temperatures*
    - *Wide temperature range (-80 to 20°C)*
    - *Wide range of discharge rates (C rate to C/400 rate)*
    - *Comparison of electrolyte types*
  - *Pulse Discharge Characterization at Various Temperatures*
  - *Current-Interrupt Impedance Measurements*

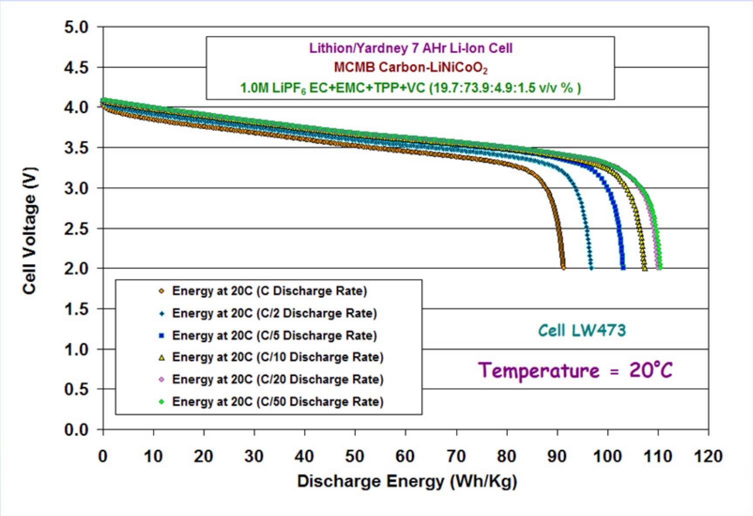


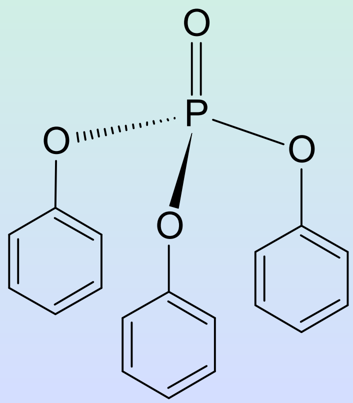
Yardney 7 Ah Prismatic Li-Ion Cells

Characterization of Cells Containing Electrolytes With FRAs

Discharge Performance at 20°C







Triphenyl phosphate (TPP)

Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M LiPF$_6$ in EC+EMC+TPP+VC*) are observed to display good performance over a range of temperatures.

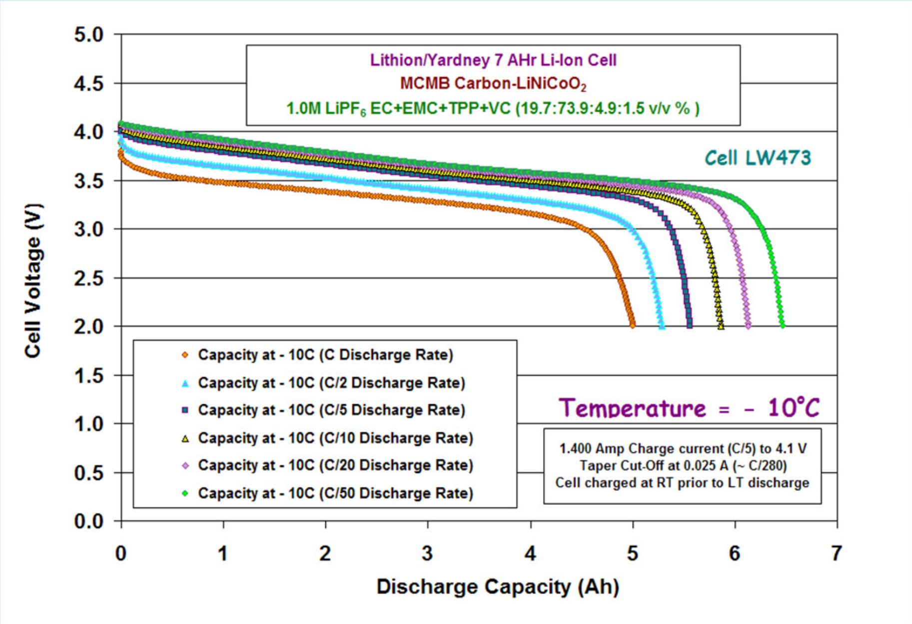
Yardney 7 Ah Prismatic Li-Ion Cells

Characterization of Cells Containing Advanced Electrolytes

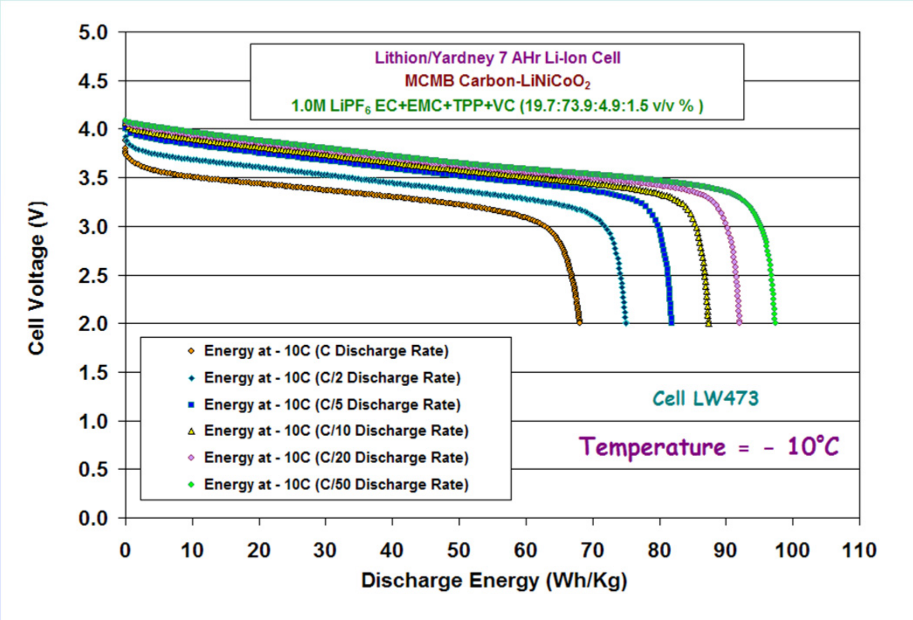
Summary of Discharge Characterization Testing at Various Temperatures

Discharge Performance at - 10°C

Discharge Capacity (Ah) at - 10°C



Discharge Energy (Wh/Kg) at - 10°C



Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M $LiPF_6$ in EC+EMC+TPP+VC*) are observed to display good performance over a range of temperatures.

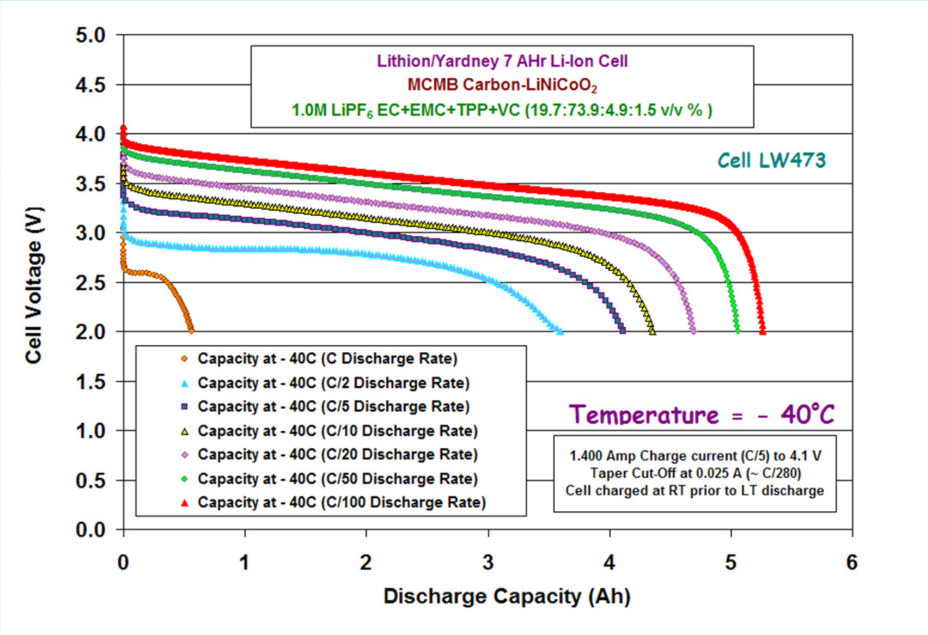
Yardney 7 Ah Prismatic Li-Ion Cells

Characterization of Cells Containing Advanced Electrolytes

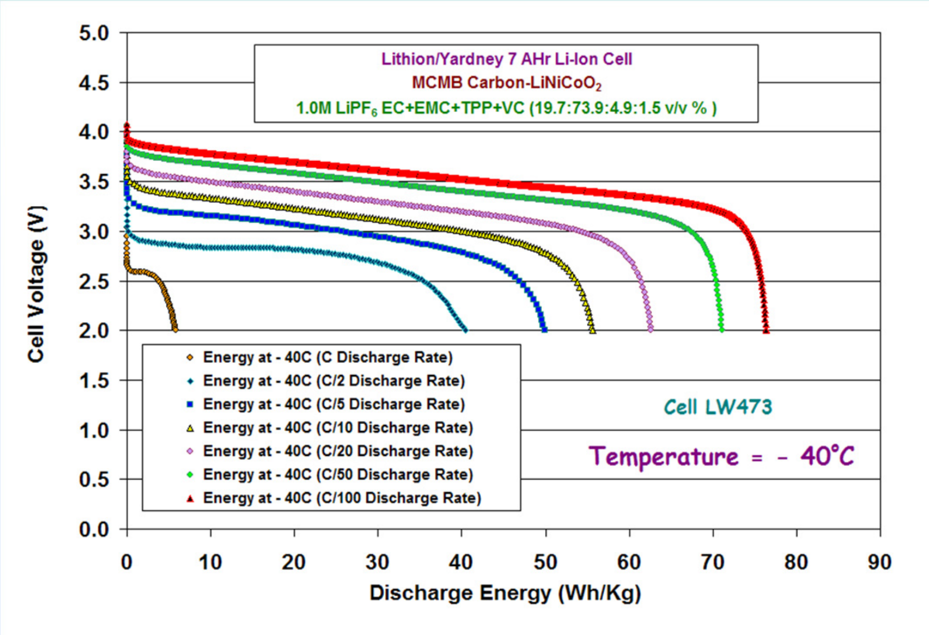
Summary of Discharge Characterization Testing at Various Temperatures

Discharge Performance at - 40°C

Discharge Capacity (Ah) at - 40°C



Discharge Energy (Wh/Kg) at - 40°C



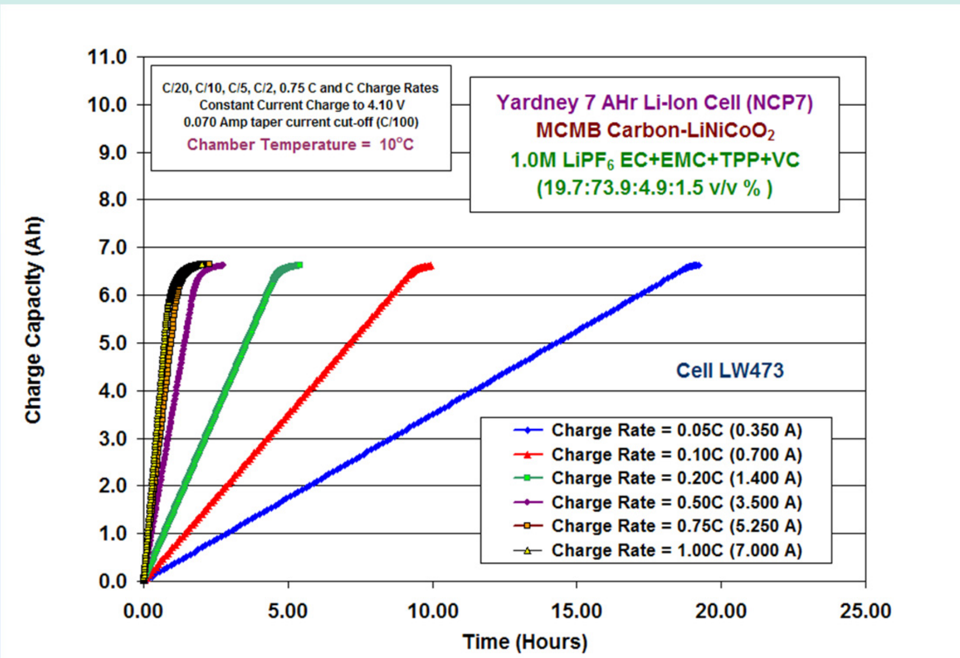
Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M $LiPF_6$ in EC+EMC+TPP+VC*) are observed to display good performance over a range of temperatures.

Yardney 7 Ah Prismatic Li-Ion Cells

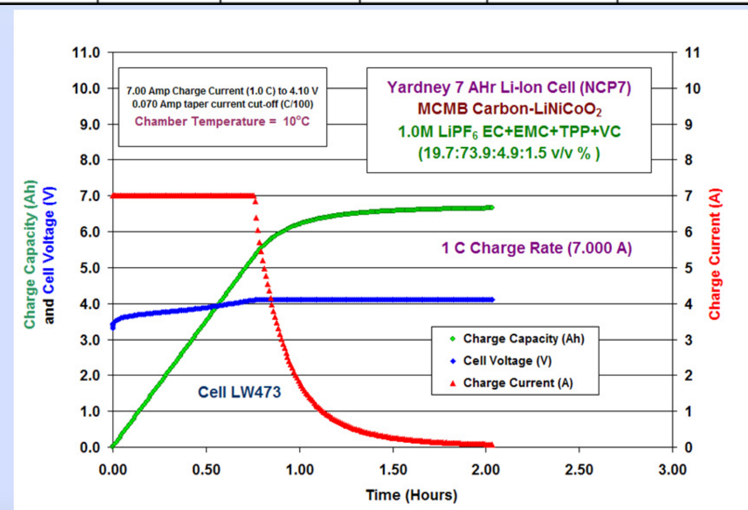
Characterization of Cells Containing Advanced Electrolytes

Charge Characteristics at 10°C

Charge Capacity (Ah)



Charge Rate	Charge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C
C/20	0.350	6.6347	19.2328	100.00	94.42
C/10	0.700	6.6185	9.9440	99.76	94.19
C/5	1.400	6.6230	5.4156	99.82	94.25
C/2	3.500	6.6205	2.7775	99.79	94.21
0.75 C	5.250	6.6541	2.2816	100.29	94.69
1.00 C	7.000	6.6553	2.0344	100.31	94.71



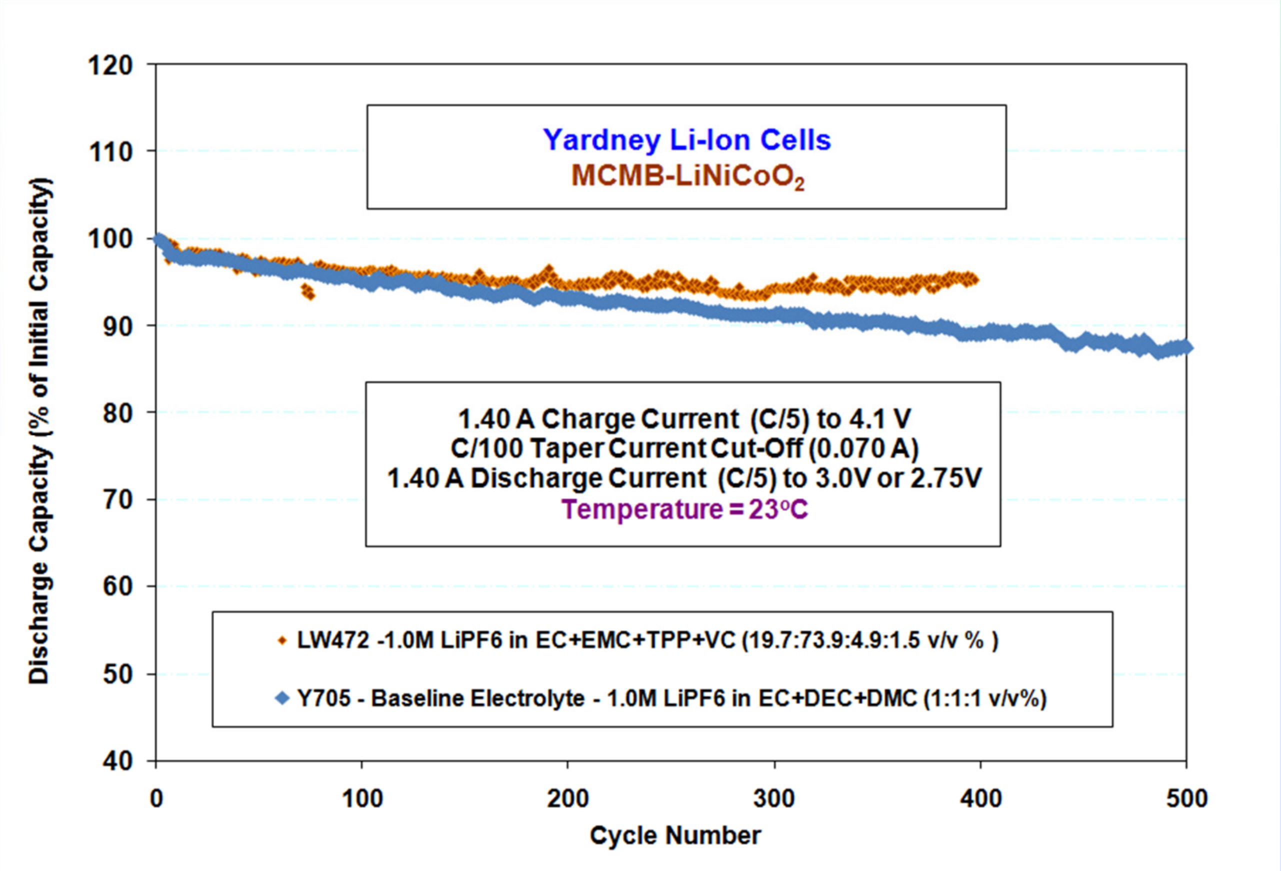
Cells were subjected to C/20, C/10, C/5, C/2 and C charge rates.
Charge rate characterization will be performed at various temperatures.

Yardney 7 Ah Prismatic Li-Ion Cells

Characterization of Cells Containing Advanced Electrolytes

100 % DOD Cycle Life Testing at Room Temperature

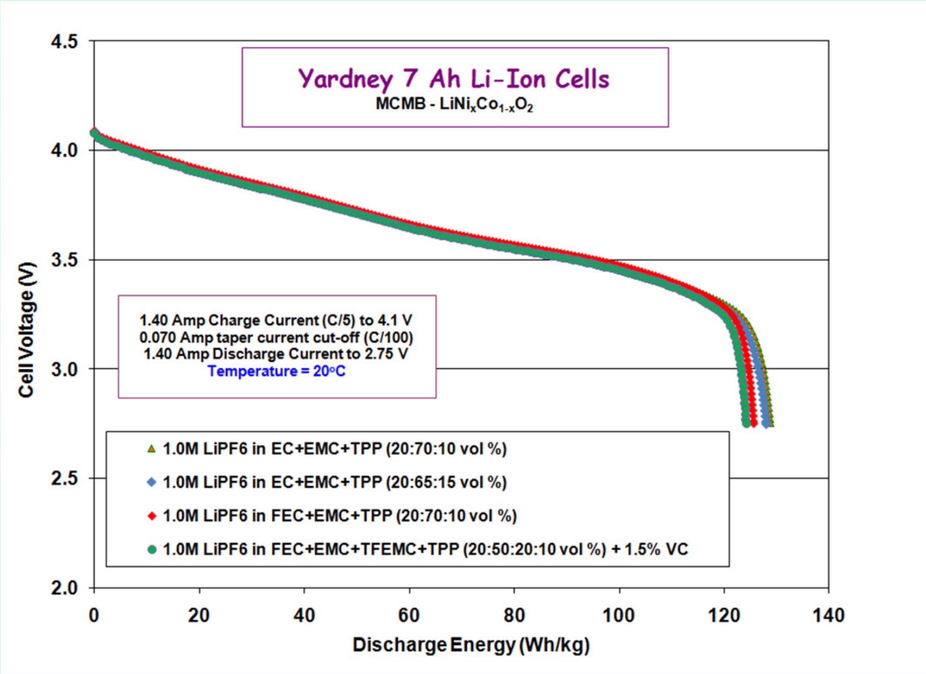
Percentage of Initial Capacity (%)

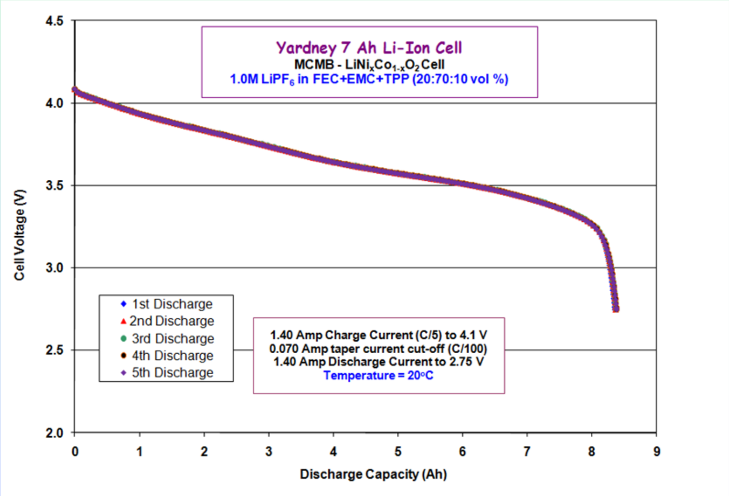


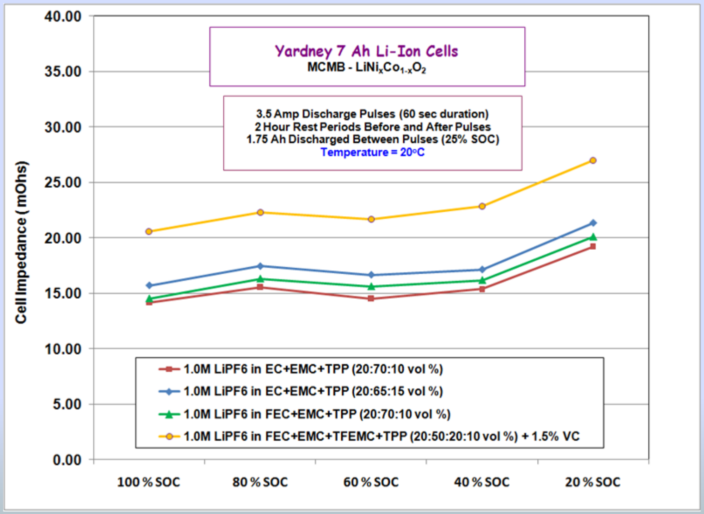
Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M $LiPF_6$ in EC+EMC+TPP+VC*) are observed to display good cycle life compared to the baseline formulation.

Discharge Characteristics MCMB / $LiNiCoO_2$ 7 Ah Cells Conditioning at 20°C

Comparison of Electrolyte Types







- We are currently evaluating a number of cells which possess electrolytes with
  (a) higher TPP content (up to 15%),
  (b) the use of FEC in lieu of EC, and
  (c) the addition of 2,2,2-trifluoroethyl methyl carbonate (TFEMC).

Initial results are very promising, suggesting good compatibility with the system.

SUMMARY and CONCLUSIONS

- ***Performance in three electrode MCMB-$LiNiCoO_2$ Cells and Graphite-$LiNiCoAlO_2$ Cells***
  - *Many electrolytes containing flame retardant additives were observed to perform well in experimental MCMB-$LiNi_xCo_{1-x}O_2$ cells.*
  - *Using electrochemical characterization techniques, the anode kinetics were more dramatically affected by the presence of FRAs compared to the cathode.*
  - *Various approaches have been taken to improve the compatibility within the systems, including using VC, FEC, LiBOB and fluorinated carbonates.*
- ***Performance in Li-$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ Coin Cells***
  - *Good performance was observed with triphenyl phosphate-containing electrolytes, however, triphenyl phosphite-based electrolytes displayed much poorer behavior.*
  - *An electrolyte consisting of 1.0M in EC+EMC+TPP (20:75:5) was shown to have the best performance or the FRA-containing electrolytes investigated.*
- ***Performance in Graphite-Toda $LiNiCoMnO_2$ Coin Cells***
  - *Many electrolyte identified as promising based on conclusions made from lithium metal anode cells performed very poorly.*
  - *This neccessited the development of further improved electrolyte aimed at improving the compatibility of the TPP-based systems (i.e., incorporation of LiBOB).*
- ***Performance in large capacity prototype MCMB-$LiNiCoO_2$ Cells***
  - *A number of electrolytes were demonstrated to have good discharge characteristics over a wide temperature range, good charge characteristics, and good life characteristics.*

Acknowledgments

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